THERMOPHYSICAL PROPERTIES OF UNDERCOOLED LIQUID AU-CU ALLOYS[1]

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ABSTRACT

The density and specific heat of liquid Au-Cu alloy above and below the liquidus temperature are investigated in a wide composition range via constant temperature and constant pressure molecular dynamics simulations. Atomic interaction of the alloy is described with embedded-atom-method (EAM). The simulated density of the Au-Cu alloy increases linearly with the decrease of temperature, whereas the specific heat keeps constant in the entire temperature range of 900-1900K. The predictions of the density and the specific heat indicate that the Neumann-Kopp's rule does not apply to Au-Cu alloy system. With the increase of gold content, the density of Au-Cu alloy increases following a two-order polynomial function, while the specific heat decreases exponentially.

KEY WORDS: Cu-Au alloys; Density; Molecular dynamic simulation; Specific heat; Undercooled liquid;

1. INTRODUCTION

Thermophysical properties of undercooled liquid alloys are important both for fundamental understanding and for industrial practice of material preparation [1,2]. Compared with pure metals, the metastable state of undercooled liquid alloys is easier to be disturbed. Furthermore, alloys are more difficult to be handled at high temperature, since whether the pre-mixing or the *in situ* alloying of the constitutional metals introduces additional experimental difficulties. Therefore, up to now, few experimental studies of thermophysical properties of undercooled liquid alloys, even for the two most important properties, i.e., density and specific heat, have been carried out. As an alternative to obtain thermophysical property experimentally, many attempts have also been made to develop predictive methods during the past several decades. Among these methods, molecular dynamics (MD) simulation method is considered to be one of the most promising methods [3,4]. In the last two decades, important progress has been made on the molecular dynamics simulation of pure metals, i.e., the transition metals [5, 6], main group metals [7], and some rare earth metals [8]. Nevertheless, due to the complexity of simulation and the lack of accurate inter-atomic potential, few works

have been done on the thermophysical properties of liquid alloys via molecular dynamics simulation method.

Au-Cu is a well-known 'model' binary alloy system, which is famous for the existence of the temperature-induced order-disorder transition, the capability of forming thermodynamically stable long period superlattice structure. In addition, three intermetallic compounds, namely Au_3Cu, AuCu, and $AuCu_3$, are of potential use in the industrial practice due to their high melting temperature, high strength, and high corrosion resistance properties. Although past researches have focused on this alloy system both experimentally and theoretically [9-12], little attention has been paid to the thermophysical properties of undercooled liquid Au-Cu alloys systematically.

The purpose of this paper is to predict the density and specific heat of liquid Au-Cu alloys in a wide composition range by molecular dynamics method. Au, Au_3Cu, AuCu, $AuCu_3$, and Cu are chosen for investigation.

2. INTER-ATOMIC POTENTIAL

The inter-atomic potential of a metal or alloy forms the basis of the molecular dynamics simulation. The embedded-atom-method (EAM) proposed by Daw and Baskes based on quasi-atom concept and density function theory [13,14] has achieved great success in describing the interaction of atoms of metals and alloys. It has been applied in the prediction of thermal expansion, surface, liquid structure, the liquid-glass transition, and crystal growth.

In the EAM, the energy of a system is subdivided into the embedding energy, i.e. the energy required to embed an atom into the local electron density due to the background atoms, and the core-core repulsion:

$$E_{tot} = \sum_i F_i(\rho_i) + \frac{1}{2}\sum_{i \neq j} \phi_{i,j}(r_{i,j}) \tag{1}$$

$$\rho_i = \sum_{i \neq j} f_j(r_{i,j}) \tag{2}$$

where E_{tot} is the total internal energy, F_i the energy for embedding atom i in an electron density ρ_i, $\phi_{i,j}$ the repulsive two-body potential between atoms i and j, $r_{i,j}$ the separation distance between atoms i and j, and $f_j(r_{i,j})$ the contribution of atom j to the electron density at atom i at a distance $r_{i,j}$ from atom j.

Recently, Barrera put forward an EAM model for Au-Cu alloys [15], which is fitted to room-temperature experimental data and takes vibrational contributions into account. This model has been applied successfully to describe the characteristics of the order-disorder transition, the structures and cohesive energies of Cu-Au alloys. According to this model, the electronic densities, the repulsive potential, and the embedding energy are represented by:

$$f_j(r) = A_j \exp(-r/\sigma_j^e) \tag{3}$$

$$\phi_{ij}(r) = B_{ij} \exp(-r_{ij}/\sigma_{ij}^r) \tag{4}$$

$$F_j(\rho_j) = -C_j\sqrt{\rho_j} \tag{5}$$

The model parameters are listed in Table 1.

Table 1. Parameters of the potential model of Au-Cu alloys

i/j	B_{ij}	σ_{ij}^r (Å)	A_i	σ_{ij}^e (Å)	C_i (eV)
Cu	7076.56	0.241535	188.542	0.536562	1
Au	14759.9	0.272639	4162.93	0.366085	1.42197
Cu/Au	10153.2	0.258268	—	—	—

3. SIMULATION DETAILS

The molecular dynamics simulations were performed in face-centered cubic boxes subject to periodical boundary conditions for systems with 500 particles. The number of gold atoms and copper atoms was assigned according to their atomic percentage in the Au-Cu alloys. During the simulation, an isothermal and isobaric ensemble was used, and the pressure was set to zero. The time step was set as 4.15 fs. In order to get equilibrium liquid state in the simulation, the system started at 1900 K, which is 544, 650, 715, 680, and 564K above the liquidus temperatures of Cu, Cu_3Au, CuAu, $CuAu_3$, and Au, respectively. This temperature was kept constant for 50,000 MD steps. Then the quenching process with a cooling rate of 4.82×10^{11}K/s was carried out to calculate the enthalpy H and density ρ at 100 K intervals of temperature. At each temperature, 30,000 steps were carried out for equilibrium. Then 20,000 additional steps were taken to calculate the enthalpy and density. The simulations were stopped at 900 K, for Cu, Cu_3Au, CuAu, $CuAu_3$, and Au, which correspond to 456, 350, 285, 320, and 436K below their respective liquidus temperatures.

During the simulation, the density of the alloy was adjusted according to the feedback of the pressure's deviation to zero. The pressure was calculated with the expression [16]:

$$P = \rho^* k_B T + \frac{1}{3V}\left\langle \sum_{i<j} r_{ij} \cdot f_{ij} \right\rangle \tag{6}$$

where ρ^* is the number density, k_B the Boltzmann constant, T the temperature, $\langle\ \rangle$ the ensemble average, r_{ij} and f_{ij} the separation and force between atom i and atom j, respectively.

Specific heat can be determined from the differential of the enthalpy:

$$C_p = dH(T)/dT \tag{7}$$

4. RESULTS AND DISCUSSIONS

Fig. 1 presents the predicted density of Au-Cu alloys versus temperature. Data

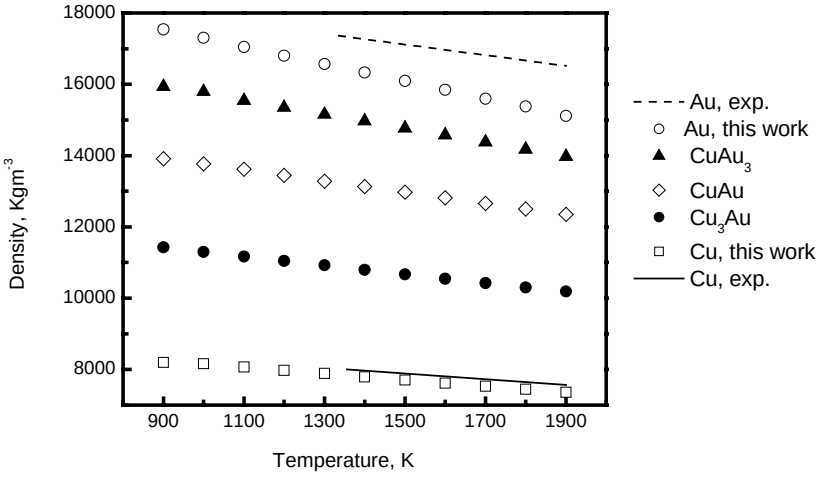

Fig. 1 Density of Au-Cu alloys versus temperature.

analysis indicates that the density of Au-Cu alloys can be represented by a linear function of temperature *T*:

$$\rho = \rho_L + \frac{d\rho}{dT}(T - T_L) \tag{8}$$

where ρ_L is the density at liquidus temperature T_L, and $\frac{d\rho}{dT}$ the temperature dependence of the density.

ρ_L, T_L, and dρ/dT of Au-Cu alloys are listed in Table 2. Obviously, both the magnitude of density and its temperature dependence increase with the increase of gold content. In order to evaluate the deviation between the prediction and the experimental data, the density of pure liquid copper and gold above their melting points from *Smithells metals reference book* [17] are also superimposed upon Fig.1. Comparisons show that the predicted results underestimate the experimental values slightly. The differences are about 2% and 5% for pure liquid copper and gold respectively. The deviations of the calculated densities of Cu_3Au, CuAu, and $CuAu_3$ alloys are not evaluated due to the lack of experimental data of liquid state.

Generally, when experimental data are not available, the density of liquid alloys is approximated from a linear interpolation of experimental data of pure elements according to the Neumann-Kopp's rule. In order to check the deviation of this approximation for Au-Cu alloys, the dependence of density on composition is shown in Fig. 2. For clarity, only the data with four temperatures, namely, 1000, 1300,1600, and

Table 2. Predicted ρ_L and dρ/dT of Au-Cu alloys

Au-Cu alloys	T_L (K)	ρ_L (kg/m^3)	dρ/dT (kg m^{-3}K^{-1})
Cu	1356	7835.9	-0.89057
Cu_3Au	1250	10982.8	-1.23933
CuAu	1185	13471.6	-1.57529
$CuAu_3$	1220	15321.4	-1.97732
Au	1336	16482.9	-2.41228

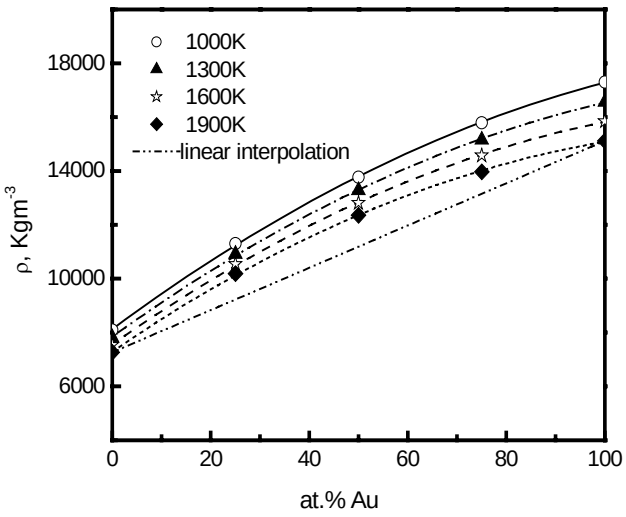

Fig. 2 Density of Au-Cu alloys at different temperatures versus Au composition.

1900K are illustrated. It can be seen from Fig.2 that ρ at any temperature can be well fitted with a two-order polynomial function of solute concentration C_{Au}. For example, ρ at 1900K can be fitted with

$$\rho = 7291.12 + 124.9545 C_{Au} - 0.4697 C_{Au}^2 \quad \mathrm{kg/m^3} \tag{9}$$

It indicates that a linear approximation is rather rough and will cause large deviation for Au-Cu alloys.

Similar to the density, the enthalpy of Au-Cu alloys is also a linear function of temperature, as illustrated in Fig. 3:

$$H_{Cu} = -5.42656 \times 10^6 + (530.03 \pm 2.97) \cdot T \quad \mathrm{J/kg} \tag{10}$$

$$H_{Cu_3Au} = -3.73887 \times 10^6 + (351.38 \pm 1.65) \cdot T \quad \mathrm{J/kg} \tag{11}$$

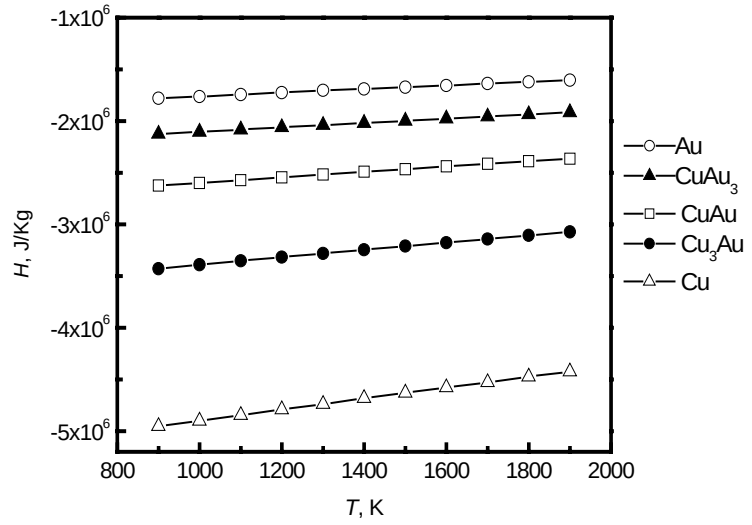

Fig. 3 Enthalpy of Cu-Au alloys versus temperature.

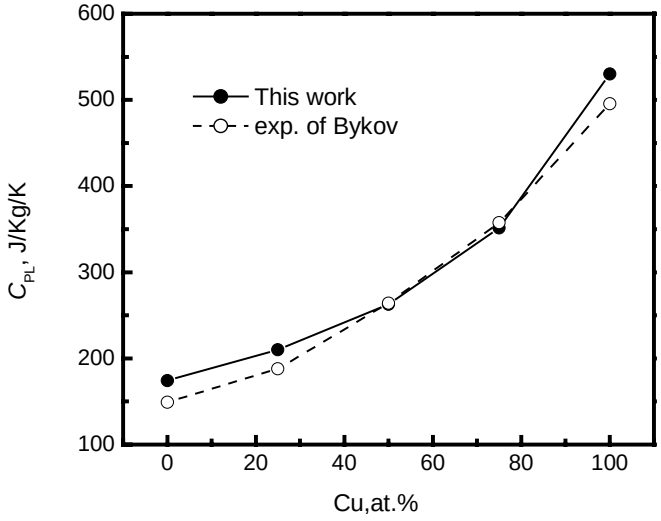

Fig. 4 Dependence on specific heats of Au-Cu alloys on the copper concentration.

$$H_{CuAu} = -2.86068\times10^{6} + (262.79 \pm 1.66)\cdot T \quad \text{J/kg} \tag{12}$$

$$H_{CuAu_3} = -2.31358\times10^{6} + (209.95 \pm 0.66)\cdot T \quad \text{J/kg} \tag{13}$$

$$H_{Au} = -1.93380\times10^{6} + (174.12 \pm 1.95)\cdot T \quad \text{J/kg} \tag{14}$$

Accordingly, the specific heats of Au-Cu alloys within the simulation temperature range are 530.03±2.97, 351.38±1.65, 262.79±1.66, 209.95±0.66, and 174.12±1.95J/kg/K, respectively. The dependence of specific heats of these five Au-Cu alloys on the copper content is given in Fig. 4. The specific heat of Au-Cu alloys increases exponentially with the increase of copper content:

$$C_{PL} = 141.16 + 36.24\exp(C_{Cu}/42.19) \tag{15}$$

In order to evaluate the specific heat predictions from MD simulation, the experimental results of Bykov [18] for normal liquid Au-Cu alloys above liquidus temperature are also shown in Fig. 4. Comparisons indicate that the predicted specific heats of CuAu and Cu_3Au alloys are in excellent agreement with the experimental results of Bykov in the normal liquid regime. The predicted results of $CuAu_3$ and Cu slightly overestimate the experimental values, with discrepancies of about 11% and 7% respectively. Despite an almost 15% overestimation of the experimental data of Bykov above the melting point, the predicted specific heat of pure liquid gold in this work is quite close to Egry's result of 165-168 $Jkg^{-1}K^{-1}$, represented by C_{PL}=177-0.00798*T J $kg^{-1}K^{-1}$, in the temperature range of 1134-1500K [19], which corresponds to an undercooling of 202K to a superheating of 164K. In Egry's experiments, the temperature dependence of specific heat of liquid gold is so small that it only leads to 1.7% variation at a temperature interval of 364K. It is not surprising that our MD simulation yields a constant value.

Like the case of density, the Neumann and Kopp's rule does not apply to the specific heats of Au-Cu alloys. This may be ascribed to the nonlinear variation of internal energy with the solute content, and the large difference of the atomic size of

copper and gold.

5. CONCLUSIONS

With molecular dynamics simulation method and an EAM inter-atomic potential model, the density and specific heat of Au-Cu alloys are studied systematically in a wide composition range. The temperature ranges from 900K to 1900K, which includes an undercooling regime of 456, 350, 285, 320, and 436K for Cu, Cu_3Au, CuAu, $CuAu_3$ and Au, respectively. Both the magnitude and the temperature dependence of the alloys' density increase with the increase of Au concentration. However, being different from Neumann-Kopp's rule, the dependence of the density of Au-Cu alloy on Au concentration follows a two-order polynomial function. Unlike the density, the specific heats of Au-Cu alloys are almost constant and show very weak temperature dependences in the whole temperature range from 900K to 1900K, which are 530.03±2.97, 351.38±1.65, 262.79±1.66, 209.95±0.66, and 174.12±1.95J/kg/K for the five Au-Cu alloys respectively. Similar to the density, the Neumann-Kopp's rule was not applicable for the specific heat of Au-Cu alloy system. The specific heat increases exponentially with the increase of Cu concentration. The predictions of density and specific heat are also compared with available experimental data. Comparisons show a reasonable agreement between the predicted and experimental data over a wide temperature and concentration variations. This indicates that the molecular dynamics simulation method can quantitatively predict thermophysical properties of liquid alloys even in the undercooled liquid regime.

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REFERENCES

[1] I. Egry, *J. Non-Crys. Solids*, **250-252**: 83 (1999).
[2] X. J. Han and B. Wei, *Phil. Mag. A*, 2003, in press.
[3] J. Miyazaki, J. A. Barker, and G. M. Pound, *J. Chem. Phys.*, **64**: 3364 (1976).
[4] A. Rahman and F. H. Stillinger, *Phys. Rev. A*, **10**: 368 (1974).
[5] J. Mei, J. W. Davenport, and G. W. Fernando, *Phys. Rev. B*, **43**: 4653(1991).
[6] R. A. Johnson, *Phys. Rev. B*, **37**: 3924 (1988).
[7] G. K. Straub, S. K. Schiferl, and D. C. Wallace, *Phys. Rev. B*, **28**: 312 (1983).
[8] G. M. Bhuiyan and M. A. Khaleque, *J. Non-Crys. Solids*, **226**: 175 (1998).
[9] L. J. Nagel, L. Anthony, and B. Futz, *Phil. Mag. Lett.*, **72**: 421 (1995).
[10] S. H. Wei, A. A. Mbaye, L. G. Ferreira, and A. Zunger, *Phys., Rev. B*, **36**: 4163 (1987).

[11] J. Cai and Y. Y. Ye, *Phys. Rev. B*, **54**: 8398 (1996).
[12] H. M. Polatoglou, and G. L. Bleris, *Solid State Commun.* , **90**: 425 (1994).
[13] M. S. Daw and M. I. Baskes, *Phys. Rev. B*, **29**: 6443 (1984).
[14] M. S. Daw and M. I. Baskes, *Phys. Rev. Lett.*, **50**: 1285 (1983).
[15] G. D. Barrera, R. H. d. Tendler, and E. P. Isoardi, *Modelling Simul. Mater. Sci. Eng.*, **8**: 389 (2000).
[16] M. D. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford university, New York, 1987), pp. 47.
[17] C. J. Smithells, *Smithells Metals Reference Book* (Butterworths, London, 1983), pp.14-6.
[18] A. Bykov and E. Pastukhov, *J. Therm. Anal. Calorim.*, **60**: 845 (2000).
[19] G. Wilde, C. Mitsch, G. P. Görler, and R. Willnecker, *J. Non-Cryst. Solids*, **205-207**: 425 (1996).